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54 Laundry detergent compositions.

57 Laundry detergent compositions containing polyamine clay  
soil removal/anti-redeposition agents are disclosed. The  
amounts of polyamine are such that the desired clay soil removal/  
anti-redeposition benefit is obtained without negatively affecting  
overall cleaning performance, even when used under stressed  
conditions.

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0206513

Laundry Detergent Compositions

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Technical Field

The present invention relates to cleaning compositions which contain low levels of certain alkoxylated polyamines. Optionally, the compositions further contain  $C_{12}$ - $C_{18}$  fatty acids; alkyl- or alkenyl- carboxylate materials, especially alkyl- or alkenyl- succinates; citric acid or citrate; polyester soil release agents; or mixtures of these optional ingredients.

Background

EP-PA 0 112 593, published July 4, 1984, describes alkoxylated amines having clay-soil removal/anti-redeposition properties when used in detergent compositions.

EP-PA 0 137 615, published April 17, 1985 describes solvent-based liquid detergent compositions containing alkoxyated polyamines. It has now been discovered that, when used at the levels exemplified in the patent literature, the alkoxyated amines may negatively affect overall cleaning performance.

It is, therefore, an object of the present invention to provide cleaning compositions which contain alkoxyated polyamine clay soil removal/anti-redeposition agents at levels high enough to provide the desired benefit, while not having or significant negative effect on other performance parameters.

#### Summary of the Invention

The present invention relates to detergent compositions designed especially for laundering fabrics. Said compositions may be formulated in liquid, solid, or granular form; the liquid form is preferred and such liquid-form compositions are hereinafter referred to as "heavy-duty liquids" or "HDL's" since they are designed to remove even the "heaviest" soil loads from fabrics when used in a conventional laundering operation.

Specifically, this invention relates to laundry detergent compositions comprising conventional deterative surfactants and, optionally, conventional deterative adjuncts, characterized in that they contain from 0.1% to 0.9 %, preferably from 0.3 % to 0.7 %, of an alkoxyated polyamine of the formula:



wherein R is hydrocarbyl having from 2 to 6 carbon atoms, R' is C<sub>1</sub> to C<sub>20</sub> hydrocarbon, alkoxy is selected from ethoxy, propoxy, butoxy, or mixtures thereof, wherein y is 2-30, n is an integer of at least 2, and X<sup>⊖</sup> is an anion.

#### Detailed description of the Invention

The present invention is based on the discovery that art-disclosed alkoxyated amine compounds, when used in detergent compositions at levels exemplified in the art, tend to negatively affect the overall cleaning performance of such compositions. The negative effects tend to occur when the detergent compositions are used under "stress" conditions, e.g. high water hardness (more than 20 gpg, or more than about 3.4 mmol Ca per liter), and/or high fabric softener load of the fabric, and/or low clay soil load.

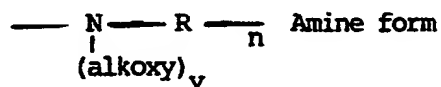
It has now been discovered that detergent compositions can be formulated which contain the alkoxy polyamine compounds at relatively low levels, whereby the intended performance benefit is obtained without causing undesirable side effects, even under "stress" conditions.

The detergent compositions are described in more detail hereinafter. All percentages and ratios mentioned in this specification are by weight, unless otherwise specified.

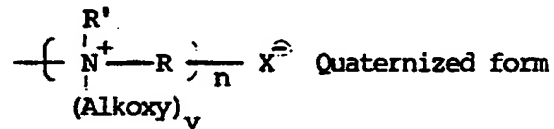
Polyamines

Alkoxyated polyamines suitable as clay-soil removal/anti-redeposition agents, as well as their preparation, are disclosed in EP-PA 0 112 593, the disclosures of which are incorporated herein by reference.

It is to be understood that the term "polyamines" as used herein represents generically the alkoxyated polyamines, both in their amine form and in their quaternarized form. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:

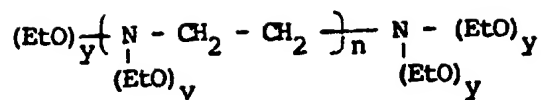


and



Wherein R is a hydrocarbonyl group, usually of 2-6 carbon atoms; R<sup>1</sup> may be a C<sub>1</sub>-C<sub>20</sub> hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X<sup>-</sup> is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene imines, i.e., the polymerized reaction product of ethylene oxide with ethylene-imine, having the general formula:



wherein n is an integer of 3 to 5 and y is an integer of 10 to 20.

Surfactants - In addition to the polyamine, the compositions herein contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such materials.

Water-soluble deterative surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkyl- and alkylether- sulfates, paraffin sulfonates, olefin sulfonates, alkoxyated (especially ethoxyated) alcohols and alkyl phenols, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, and the like, which are well-known from the detergency art. In general, such deterative surfactants contain an alkyl group in the C<sub>9</sub>-C<sub>18</sub> range; the anionic deterative surfactants are most commonly used in the form of their sodium, potassium or triethanolammonium salts; the nonionics generally contain from about 5 to about 17 ethylene oxide groups. U.S. Patent 4,111,855 contains detailed listings of such typical deterative surfactants. C<sub>11</sub>-C<sub>16</sub> alkyl benzene sulfonates, C<sub>12</sub>-C<sub>18</sub> paraffin-sulfonates and alkyl sulfates, and the ethoxyated alcohols and alkyl phenols are especially preferred in the compositions of the present type.

The surfactant component can comprise as little as 1 % of the compositions herein, but preferably the compositions will contain 1 % to 40 %, preferably 5 % to 30 %, of surfactant. Mixtures of the ethoxylated nonionics with anionics such as the alkyl benzene sulfonates, alkyl sulfates and paraffin sulfonates are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabrics.

Fatty Acid/Soap Ingredient - Fatty acids (generally  $C_{12}$ - $C_{18}$  chain length) and their water-soluble salts (i.e., common "soaps", especially alkali metal soaps) can be used in the present compositions not only for their deterative surfactant properties, but also to provide an additional detergency builder function by virtue of their ability to interact with water hardness cations. For these reasons, the fatty acids are highly desirable components of the compositions herein. They are typically used at 5-30 % by weight of the composition.

Optional Ingredients - The compositions herein can contain other ingredients which aid in their cleaning performance. For example, it is highly preferred that detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, silicates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino polyphosphonates and phosphates (DEQUEST) and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent

3.579.454 for typical examples of the use of such materials in various cleaning compositions. In general, the builder/sequestrant will comprise about 0.5 % to 15 % of the composition. Citrate is one of the most preferred builders since it is readily soluble in the aqueous phase of heavy-duty liquid detergent compositions.

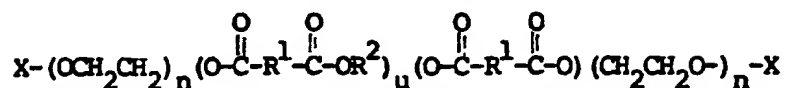
Other examples of suitable builders are those of the general formula  $R-CH(COOH)CH_2(COOH)$  i.e. derivatives of succinic acid, wherein R is  $C_{10}-C_{20}$  alkyl or alkenyl, preferably  $C_{12}-C_{16}$ , or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include: lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyl succinate (preferred), 2-pentadecenyl succinate, and the like.

The compositions herein also preferably contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial deterative enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions. Ingredients such as propane diol and/or formate, calcium and boric acid, can be added to help stabilize the enzymes in well-known fashion, according to the desires of the formulator.

The compositions herein also preferably contain soil release polymers having the generic formula :



in which X can be any suitable capping group, with each X being selected from the group consisting of H, and alkyl or acyl groups containing from 1 to about 4 carbon atoms, in particular methyl. n is selected for water solubility and generally is from about 6 to about 120, preferably from about 10 to about 50. u is critical to formulation in a liquid detergent having a relatively high ionic strength. There should be little material, preferably, less than 5%, having u greater than 5. Furthermore, the weight average value of u preferably is in the range of from 1 to 2.

The  $R^1$  moieties are essentially 1,4-phenylene moieties. As used herein, the term "the  $R^1$  moieties are essentially 1,4-phenylene moieties" refers to compounds where the  $R^1$  moieties consist entirely of 1,4-phenylene moieties, or are partially substituted with other arylene or alkarylene moieties, alkylene moieties, alkenylene moieties, or mixtures thereof. Arylene and alkarylene moieties which can be partially substituted for 1,4-phenylene include 1,3-phenylene, 1,2-phenylene, 1,8-naphtylene, 1,4-naphtylene, 2,2-biphenylene, 4,4-biphenylene and mixtures thereof. Alkylene and alkenylene moieties which can be partially substituted include ethylene, 1,2-propylene, 1,4-butylene, 1,5-pentylene, 1,6-hexamethylene, 1,7-heptamethylene, 1,8-octamethylene, 1,4-cyclohexylene, and mixtures thereof.

For the  $R^1$  moieties, the degree of partial substitution with moieties other than 1,4-phenylene should be such that the soil release properties of the compound are not adversely affected to any great extent. Generally, the degree of partial substitution which can be tolerated will depend upon the backbone length of the compound, i.e., longer backbones can have greater partial substitution for 1,4-phenylene moieties. Usually, compounds where the  $R^1$  comprise from about 50 to 100 % 1,4-phenylene moieties (from 0 to about 50 % moieties other than 1,4-phenylene) have adequate soil release activity. For example, polyesters made according to the present invention with a 40:60 mole ratio of isophthalic (1,3-phenylene) to terephthalic (1,4-phenylene) acid have adequate soil release activity. However, because most polyesters used in fiber making comprise ethylene terephthalate units, it is usually desirable to minimize the degree of partial substitution with moieties other than 1,4-phenylene for best soil release activity. Preferably, the  $R^1$  moieties consist entirely of (i.e., comprise 100 %) 1,4-phenylene moieties, i.e. each  $R^1$  moiety is 1,4-phenylene. (Irrespective of the mechanism of action, it is surprising that the soil release polymers do show excellent benefits on fabrics other than polyester fabrics and the compositions herein are designed to clean all manner of fabrics and textiles.)

For the  $R^2$  moieties, suitable ethylene or substituted ethylene moieties include ethylene, 1,2-propylene, 1,2-butylene, 1,2-hexylene, 3-methoxy-1,2-propylene and mixtures thereof. Preferably, the  $R^2$  moieties are essentially ethylene moieties, 1,2-propylene moieties or mixtures thereof. Inclusion of a greater percentage of ethylene moieties tends to improve the soil release activity of the compounds. Surprisingly, inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of the compounds.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleaches, optical brighteners, soil suspending agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach activators and the like.

In a through-the-wash laundry mode, the compositions are typically used at a concentration of at least 500 ppm, preferably 0.10 % to 2.5 %, in an aqueous laundry bath at pH 7-11 to launder fabrics. The laundering can be carried out by agitating fabrics with the present compositions over the range from 5°C to the boil, with excellent results.

In the examples of heavy duty liquid detergents the following abbreviations are used :

HLAS	linear alkyl benzene sulfonic acid
AS	alkyl sulfate (TEA salt)
TEA	triethanolamine
EA(x)EO(Y)	nonionic; ethoxylated alcohol having an alkyl chain of x carbon atoms and an average degree of ethoxylation of Y.
DETPMP	diethylenetriamine penta(methylene phosphonate)
TWCFA	topped, whole cut coconut fatty acid
Soil release polym.	prepared by esterifying 1,4 phthalic acid (chloride) with 1,2-propane diol and ethoxylating the polymer with

ethylene oxide. The amounts of reactants are chosen so as to result in a polymer having an average u value in the range of from 1 to 2, and an average degree of ethoxylation (n value) in the range of from 12 to 43.

Polyamine

A polyamine clay soil removal/antiredeposition agent of the formula defined hereinabove.

Alk. Succ.

mixed C<sub>12</sub>-C<sub>14</sub> alkenyl succinate

Minors

include dye, perfume, opacifier, anti-oxidant, brightener, suds suppressor, etc.

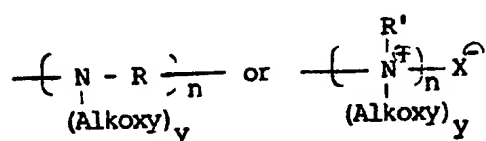
EXAMPLES I - VI

	I	II	III	IV	V	VI
<u>Ingredient</u>	<u>Percent (Wt)</u>					
HLAS	11	12	6	14	8	10
AS	4	4	8	-	5	6
TEA	5	4	6	4.5	8	3
NaOH	3.5	4	2	3.5	1	4
EA(12-15) (EO(7)	12	10	13	18	8	12
Ethanol	6	5	8	5	3	6
Propanediol	1.5	3	-	2	6	2
Na formate	1	0.8	-	1.5	0.5	1
DETPMP	1.7	2	1	2	0.5	1.7
Citric acid	0.9	1	-	0.5	2	0.9
TWCFA	11	-	12	2	8	11
Oleic acid	4	-	5	1	7	4
Soil Release Polym.	0.5	-	0.3	0.2	-	-
Polyamine	0.3 <sup>1)</sup>	0.7 <sup>2)</sup>	0.5 <sup>3)</sup>	0.7 <sup>4)</sup>	0.4 <sup>5)</sup>	0.5 <sup>6)</sup>
Alk. Succ.	-	20	-	15	-	-
protease	0.4	0.5	-	0.2	0.3	0.4
Amylase	0.1	-	-	0.2	0.1	0.1
Water + Minors	-----balance-----					

- 1)  $n = 4; y = 15; R = \text{ethylene} ; \text{alkoxy} = \text{ethoxy}$
- 2)  $n = 20; y = 30; R = \text{propylene} ; \text{alkoxy} = \text{propoxy}$
- 3)  $n = 3; y = 15; R = \text{ethylene} ; \text{alkoxy} = \text{ethoxy} ; R' = \text{butyl}$
- 4)  $n = 5; y = 9; R = \text{butylene} ; \text{aloxo} = \text{butoxy}$
- 5)  $n = 20; y = 10; R = \text{hexylene} ; \text{aloxo} = \text{ethoxy} ; R' = \text{dodedyl}$
- 6)  $n = 3; y = 20; R = \text{ethylene} ; \text{alkoxy} = \text{ethoxy} ; R' = \text{eicosyl}$

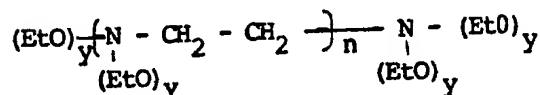
Claims

1. A laundry detergent composition comprising conventional deterative surfactants, and optional, conventional deterative adjuncts, characterized in that it contains :  
from 0.1 % to 0.9 % of an alkoxyated polymaine of the formula :



wherein R is hydrocarbyle having from 2 to 6 carbon atoms, R' is C<sub>1</sub> to C<sub>20</sub> hydrocarbon, alkoxy is selected from ethoxy, propoxy, butoxy, or mixtures thereof, y is 2-30, n is an integer of at least 2, and X<sup>⊖</sup> is an anion.

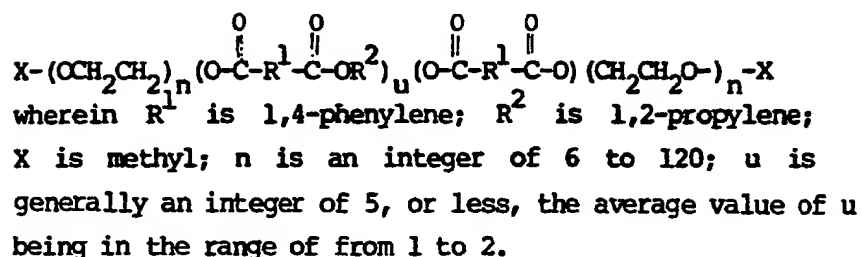
2. A composition according to Claim 1 wherein the alkoxyated polyamine is the polymerized reaction product of ethylene oxide with ethylene imine.
3. A composition according to Claim 2 wherein the alkoxyated polyamine is of the formula :



wherein n is an integer from 3 to 5 and y is an integer from 10 to 20.

4. A composition according to any of the preceding claims which further comprises from 5 % to 30 % of C<sub>12</sub>-C<sub>18</sub> fatty acids.

5. A composition according to any of the preceding claims which further comprises from 0.01 % to 2.5 %, preferably from 0.1 % to 1 %, of the soil release polymer defined herein.
6. A composition according to claim 5 wherein the soil release polymer is of the formula :



7. A composition according to any of the preceding claims which further comprises from 1 % to 35 % of an alkyl- or alkenyl dicarboxylate detergency builder.
8. A composition according to Claim 7 wherein the dicarboxylate builder is a  $C_{12}$ - $C_{16}$  alkyl- or alkenyl-succinate.
9. A composition according to any of the preceding claims which further comprises from 0.1 % to 3 % of citric acid or a salt thereof.
10. A liquid detergent composition according to any of the preceding claims.

11. A composition according to any of the preceding claims which comprises from 0.3 % to 0.7 of the polyamine.
12. A method of laundering fabrics by agitating fabrics with an aqueous bath containing at least 500 ppm of a composition according to one of the foregoing claims.



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# EUROPEAN SEARCH REPORT

0206513  
Application number

EP 86 30 3780

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, X	EP-A-0 137 615 (PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER) * page 7, paragraph 2, example 3, claims 1-3, 6 *	1, 2, 9, 10	C 11 D 3/30 C 11 D 1/44 C 11 D 3/00
D <sup>A</sup>	--- EP-A-0 112 593 (THE PROCTER & GAMBLE CO.) * page 38, line 27, claim 1 *		
A	--- EP-A-0 111 984 (THE PROCTER & GAMBLE CO.) * abstract, claim 1 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 11 D 3/00 C 11 D 1/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 11-08-1986	Examiner SCHULTZE D
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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